## Short Communication

# Dication–Nucleophile Combination. The Reactions of 2,6-Bis(*N,N*-dimethylamino)anthracene Dication with Nucleophiles

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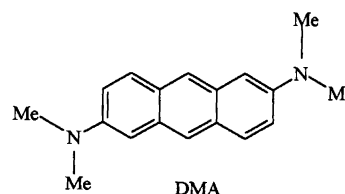Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, USA

Although radical cation–nucleophile combination reactions have been investigated in detail,[1-14] organic dication–nucleophile combinations have received little attention. Dications have been implicated as intermediates in some radical cation–nucleophile reactions[1] and it has been known for a long time[15] that dications are generally more reactive than the corresponding radical cations by factors as great as about $10^6$. The high reactivity of both radical cations and dications toward nucleophiles makes it difficult to find suitable dication–nucleophile combination reactions to study. A possible approach to this problem is to make the site of attack by the nucleophile sufficiently sterically hindered so that the radical cation reaction is very slow, which would allow direct electrochemical studies to be carried out on the corresponding reaction of the dication. An undesirable feature of this approach is that the observed dication reactivities would be controlled to a large extent by steric effects, possibly masking electronic effects. We chose instead to study anthracene dications substituted by electron donating substituents at positions remote from the site of nucleophilic attack.

The anodic oxidation of 2,6-bis(*N,N*-dimethylamino)-anthracene (DMA) in acetonitrile–$Bu_4NPF_6$ (0.1 M) in the presence of $Bu_4NOAc$ resulted in products derived from the initial attack of acetate ion on the 9-position of the dication as expected from previous studies of anthracene radical cation–nucleophile combination reactions.[12]
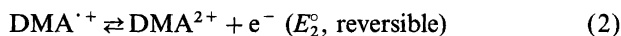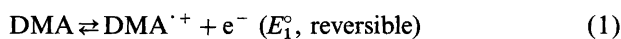
We found that the kinetics of the reactions between the DMA dication and substituted pyridines as nucleophiles can readily be studied by derivative cyclic voltammetry. The site of nucleophilic attack on $DMA^{2+}$ by

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nitrogen-centered nucleophiles, in analogy to the reaction with acetate ion, is the unhindered 9-position. These nucleophiles were selected in order to compare the relative reactivities of $DMA^{2+}$ with those observed for one of the most highly studied radical cations, that from 9-phenylanthracene.



DMA

The cyclic voltammogram for the oxidation of DMA in dichloromethane–$Bu_4NPF_6$ (0.5 M) at a voltage sweep rate (*v*) of 200 mV s$^{-1}$ is shown in Fig. 1. Two consecutive charge transfers with a difference in $E_{rev}$ for the two processes of close to 130 mV were observed at sweep rates ranging from 0.2 to 20 V s$^{-1}$. In the presence of pyridine, the peak current for the reduction of the dication ($R_2$) was observed to be dependent upon *v* diminishing at low *v*. This observation suggested that the kinetics of the reaction between $DMA^{2+}$ and pyridine could be studied by derivative cyclic voltammetry (DCV).

Theoretical data for the dication reactions were obtained by digital simulation[16] of reactions (1)–(4). The ratio of the derivative peak currents ($R'_i$) for the second redox couple plotted vs. the dimensionless rate constant, λ [eqn. (5)], provided a theoretical working curve with which to compare experimental DCV data.

$$DMA \rightleftharpoons DMA^{\cdot+} + e^- \quad (E_1^\circ, \text{ reversible}) \qquad (1)$$

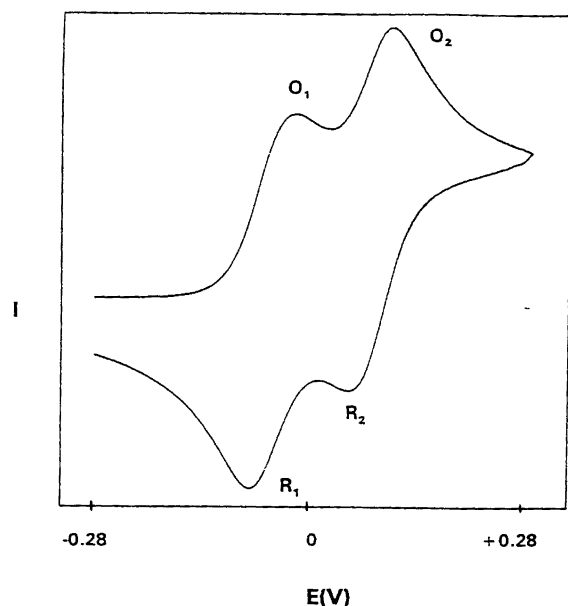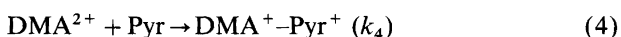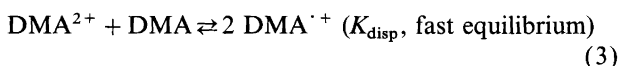$$DMA^{\cdot+} \rightleftharpoons DMA^{2+} + e^- \quad (E_2^\circ, \text{ reversible}) \qquad (2)$$

*Fig. 1.* Cyclic voltammogram for the oxidation of 2,6-bis($N,N$-dimethylamino) anthracene in dichloromethane–$Bu_4NPF_6$ (0.5 M) at a voltage sweep rate of 200 mV s$^{-1}$. The potential scale is referred to ferricenium/ferrocene ($Fc^{+}/Fc$).

$$DMA^{2+} + DMA \rightleftarrows 2\ DMA^{\cdot+} \quad (K_{disp}, \text{ fast equilibrium})$$
$$(3)$$

$$DMA^{2+} + Pyr \rightarrow DMA^{+}-Pyr^{+} \quad (k_4)$$
$$(4)$$

$$\lambda = RTk_4C^{\circ}/nFv$$
$$(5)$$

In eqn. (5), $C^{\circ}$ is the substrate concentration and the other symbols have their usual meanings. Experimental $R'_I$ data were plotted as a function of $\log \lambda$ and pseudo-first-order rate constants were obtained from which the second-order rate constants for the dication–nucleophile combinations could be calculated. The theoretical working curve, along with experimental data for the reaction of $DMA^{2+}$ with pyridine at 21 °C, is illustrated in Fig. 2.
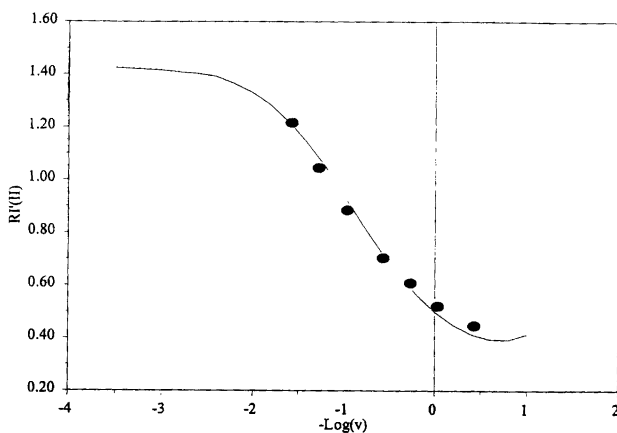


*Fig. 2.* Theoretical working curve for the reactions of $DMA^{2+}$ with nucleophiles (solid line). The experimental data (solid circles) are for the reaction of $DMA^{2+}$ with pyridine at 21 °C.

Kinetic data for the reactions of $DMA^{2+}$ with a series of nitrogen-centered nucleophiles are summarized in Table 1. Data for pyridine, 4-methylpyridine and 4-cyanopyridine show, as expected, that the rate of the reaction is enhanced by the presence of electron-donating substituents and decreased by the presence of electron-withdrawing substituents on the 4-position of the pyridine ring. These limited data give rise to a Hammett $\rho$ of $-3.15$ ($r^2 = 0.9999$). The presence of substitutents in the 2- or 2,6-positions gives rise to a substantial decrease in the observed rate constants.

The last column in the table summarizes the relative second-order rate constants for the reactions of 9-phenylanthracene radical cation (9-PA$^{\cdot+}$) with the nitrogen centered nucleophiles. Very similar trends in the relative rate constants were obtained for several substituted anthracene radical cations.[9] The most interesting feature of the data in the table is that although $DMA^{2+}$ is nearly three orders of magnitude less reactive toward the nucleophiles than is 9-PA$^{\cdot+}$, the dication is less selective than the radical cation by one to two orders of magnitude. By selectivity we mean the second-order rate constant relative to that for the reaction with 2,6-dimethylpyridine.

Rate constants were measured as a function of temperature ($-40$ to 30 °C) for the reaction of $DMA^{2+}$ with pyridine in dichloromethane–$Bu_4NPF_6$ (0.5 M). A plot of $\log k$ vs. $1/T$ shows a maximum value of $\log k$ near 20 °C and is very nearly linear between 10 and $-30$ °C. The Arrhenius activation energy calculated for the latter temperature range is equal to 4.6 kcal mol$^{-1}$. This also contrasts the behavior of radical cations with pyridine which exhibit negative or near zero Arrhenius activation energies.[9] The non-linear Arrhenius behavior suggests that the $DMA^{2+}$–pyridine reaction may not follow a simple-single step second-order reaction pathway. More detailed studies on this and other dication–nucleophile combinations are necessary before drawing mechanistic conclusions.

We have shown here that the kinetics of dication–nucleophile combination reactions can readily be studied

*Table 1.* Second-order rate constants for the reactions of 2,6-bis($N,N$-dimethylamino)anthracene dication with nitrogen-centered nucleophiles in dichloromethane–$Bu_4NPF_6$ (0.5 M) at 21 °C.

| Nucleophile | log ($k$/dm$^3$ mol$^{-1}$ s$^{-1}$) | $k_{rel}$[a] | $k_{PA}$[b] |
|---|---|---|---|
| 4-Methylpyridine | 4.47 | 1514 | 36300 |
| Pyridine | 4.32 | 1072 | 10900 |
| 2-Methylpyridine | 2.39 | 12.6 | 1000 |
| 4-Cyanopyridine | 2.09 | 6.31 | 661 |
| 2,6-Dimethylpyridine | 1.29 | 1.00 | 1.00 |
| 2-Cyanopyridine | 1.09 | 0.63 | — |

[a]Second-order rate constant relative to that for reaction with 2,6-dimethylpyridine. [b]Relative second-order rate constants for the reactions of the nucleophiles with 9-phenylanthracene radical cation.[9]

using electrochemical techniques. Work in progress is aimed at making detailed kinetic comparisons between radical cation and dication reactions and is expected to identify the factors responsible for the differences in reactivities of the two classes of reactive intermediates.

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